Studies on promotional effect of electrode surface modifications in photoelectrochemical water splitting

Synopsis of the work proposed for the award of Ph.D. degree in Chemistry

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1. Introduction

Energy demand of the world is rising at an unprecedented rate. To meet this burgeoning requirement, the greater exploitation of nonrenewable sources of energy, viz. coal, petroleum, natural gas and oil, provide only a short term respite; as all the estimates suggest that the rate at which the conventional fuel reserves are being depleted, the time is not too far when these would be completely exhausted. Besides, the unabated combustion of conventional fuels has also resulted in multifarious adverse effects on environment. In this scenario, non-renewable energy offers probably the only long-lasting solution for a secured, affordable, clean and equitable energy supply in future. Amongst all available renewable energy options, solar energy is the most significant, since it is endlessly incident on earth's surface. The yearly flux of solar energy on earth's surface is about 3 $\times 10^{24}$ J, which is much higher than the total consumption of energy worldwide (roughly estimated to be10^{4} J). So, if only a small fraction of the total solar flux is tapped, that itself would suffice to meet the total energy requirements of the world (Centi et al., 2010).

Capturing solar energy and storing it to directly usable chemical fuel viz. hydrogen, via photoelectrochemical (PEC) splitting of water, has drawn much interest in recent years. The

phenomenon of PEC water splitting was first reported in the year 1972 (Fujishima and Honda, 1975). Since then many semiconductors have been investigated for this application, yielding significant advancement in the knowledge and our understanding to the phenomenon. It is also a fact that among all the available methods/technologies for water splitting, PEC route is the most promising on account of it being a single step energy-conversion and its ease of operation (Bak et al. 2002). PEC cell device contains a light-absorbing semiconductor photoelectrode and an auxiliary electrode, both soaked in a suitable electrolyte solution. On exposure to the sunlight, electron-hole pairs are created in the semiconductor electrode, and separated in the space charge field. With an n-type semiconductor electrode (which would work as anode) photo-excited holes drive the oxygen-evolution reaction. At the same time, photo-excited electrons participate in the hydrogen-evolution reaction at the cathode auxiliary electrode (Fig. 1). With a p-type semiconductor, the direction of flow of charge carriers (i.e. electrons and holes) is reverse.

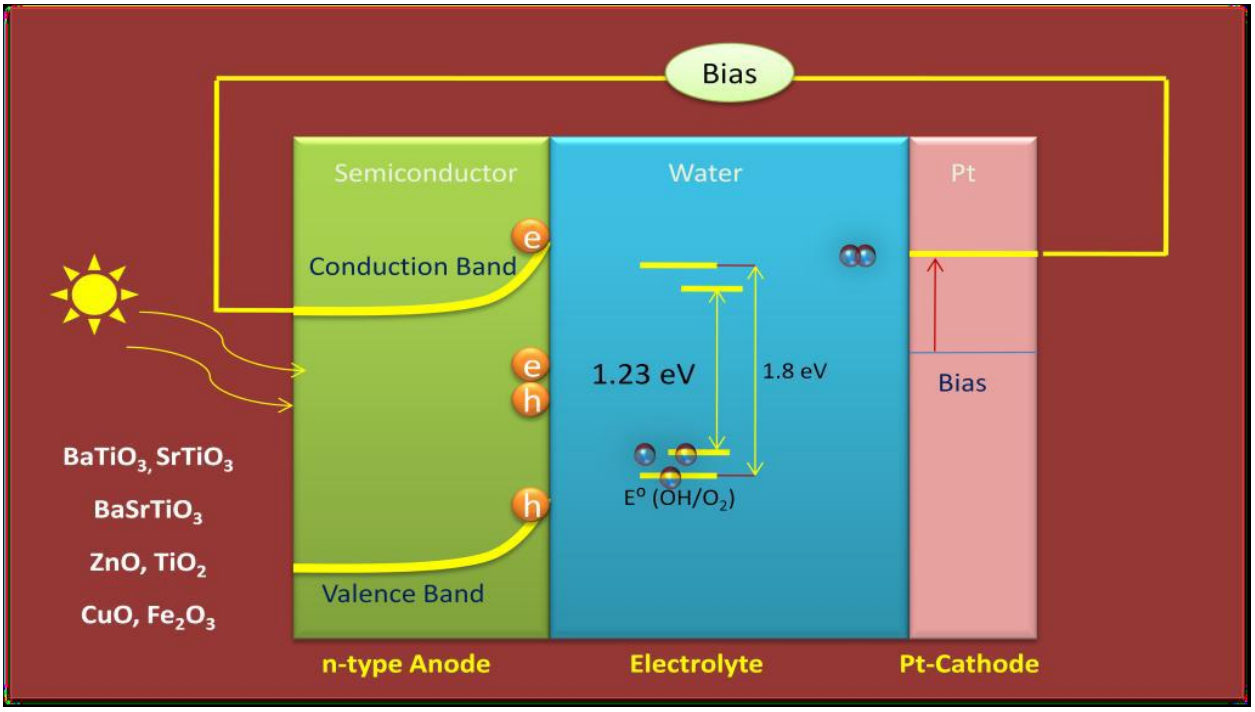

Fig. 1: Schematics of a PEC cell with n-type semiconductor electrode (Google Images)

Thermodynamically water cannot be split spontaneously under ambient conditions and, for the reaction to progress, it requires an energy input of nearly 1.8 eV (including the PEC cell over-voltage losses) (Akkerman et al., 2002). Additionally, following requirements need to be met: (i) optical matching of the solar spectrum with the absorption response of the material (ii) efficient separation of photo-generated charge carriers (i.e. electrons and holes) at the semiconductor-electrolyte junction, and (iii) the chemical stability of electrode under illumination and in contact with electrolyte solution ((Hisatomi et al., 2014).). Thus, the efficiency of PEC cell for hydrogen generation hinges critically upon material properties of the semiconductor used as photoelectrode (Bak et al., 2002). In the past, many studies were conducted to explore the PEC performances of different semiconductors, including doped systems, mixed oxides, bi- and multi-junction systems for water splitting (Venkata et al., 2011). Further, the growth of nanoscience and nanotechnology in recent years has led to a renewed interest even in such materials that may be referred as old work horses, viz. oxides of iron, zinc and copper etc., as there are clear evidences to suggest that with the unique evolution of microstructure and enhnced surface area in nanostructured/nanocrystalline state, these materials may offer higher PEC response.

Mechanistically, the PEC splitting of water is a phenomenon in which surface characteristics of the semiconductor electrode, especially at the semiconductor-electrolyte junction are most crucial. Upon illumination, the photo-generated charge carriers, which tend to accumulate on the surface of the semiconductor, may also initiate undesired reaction pathways viz. surface corrosion and other photo-response inhibiting parallel reactions. By inducing appropriate surface modifications, and enabling fast separation and migration of charge carriers (i.e. electrons and holes), the probability of occurrence of undesired reactions/reaction pathways can be reduced. Thus, in the continued search for an efficient semiconductor system for PEC water splitting, optimization of surface characteristics of the semiconductor electrode is seemingly the most crucial step.

There can be different facets of electrode surface modifications. These would include, but not limited to, controlled surface etching; surface deposition of metals/metal islands; and surface loading of sensitizers/catalysts. As said before, PEC photocurrent basically depends upon the outcome of the two competitive processes, i.e. interfacial charge transfer and electron–hole recombination. So, the major objectives behind electrode surface modification are: (i) to increase the absorption of light radiations falling on the electrode surface and (ii) to facilitate the electron-hole separation and limit the recombination losses. In the past, dye-sensitized PEC cells (fabricated by using thin films of semiconductors), have been investigated in great detail. In such studies, researchers have explored the use of different organic compounds/dyes (coated/deposited on the surface of mostly high band gap semiconductor) for their role as sensitizer to the process; wherein the extension of light absorption to longer wavelengths (i.e. visible light) had been the main objective. The use of organic semiconductors, in tandem with metal oxide semiconductors, to evolve junction nano-hetero-structures for efficient PEC water splitting, remains a scantily studied aspect so far. In a study where deposition of porphyrins onto a p-$GaInP_2$ electrode was attempted and then followed by etching with concentrated sulfuric acid, the results showed an increase in photocurrent (Varner et.al, 2002). Surface modification by planting/decorating semiconductor surface with metal nanoparticles is also known to enhance the efficiency of water splitting. However, in this modification non-uniform deposition of metals on the semiconductor surface is desired, as thick uniform metal layer may actually inhibit the process by blocking the light absorption by semiconductor. Another interesting approach towards the surface modification of semiconductor electrodes is the use of swift heavy ions (SHI). In this method, the penetrating heavy ions enter into material layers and create disordered zone along its trajectory. It leads to varied changes in the microstructure of the material, which may be optimized to generate efficient PEC electrode (Su et.al, 2011).

It is also apparent from the literature survey that most of the semiconductors investigated for PEC water splitting so far are inorganic in nature. Compared to that we find only limited work reported on the use of organic materials/semiconductors for this purpose (Young et.al, 2005). Polymers are macromolecules formed by the repetitive union of a large number of reactive small molecules in a regular sequence. Polymers have long been used as insulating materials, but now they have become the most versatile in terms of their applications. This is due to few unique advantages that they have over many other materials, such as flexibility, tailorability, processability, and stability. The versatility of polymeric materials has expanded to their use as electrochemical materials as well. Intrinsically conductive polymers (ICP) represent a class of polymers, having conjugated double bonds (Table 1). Different derivatives of polyacetylene, polyaniline, polypyrrole, and polythiophene are few of the examples of this category (Gauthier et. al, 1988). Owing to their high electrical conductivity, such polymers are also known as "synmet" or "synthetic metal". With the presence of the chain of sp^2 hybridized carbon atoms, there would occur alternate single and double bonds throughout the chain. The pi-electrons of the unhybridized p-orbitals (one orbital corresponding to each carbon atom) remain delocalized throughout the polymer chain. It is also to be noted here that the conductivity of conductive polymers decreases with falling temperature in contrast to the conductivity of typical metals.

Table 1

Few polymers with their reported bandgap and conductivity values.

Polymer type (including derivatives)	Tentative Band gap (eV)	Conductivity (S/cm)
Polyacetylene	1.5	$10^3 – 1.7 \times 10^5$
Polypyrrole	3.1	$10^2 – 7.5 \times 10^3$
Polythiophene	2.0	$10 – 10^3$
Polyphenylene	3.0	$10^2 – 10^3$
Polyaniline	3.2	30 – 200

Source.: Dai, L. (1999) J. Macromol. Sci., Rev. Macromol. Chem. Phys. C **39**, 273.

2. Genesis of the Proposal

It is apparent from the literature survey that none of the semiconductors investigated so far are able to meet all the requirements for efficient and viable PEC water splitting. Owing to this realization, in recent years, one can notice lot of emphasis being laid on the synthesis and use of nano-hetero-structures for this application. In such systems, the idea is to exploit the individual advantages of different materials by generating bi-layered and multi-layered structures (mostly in the form of thin films coated on a suitable substrate). Here again, we find that the interfacing of the inorganic materials/semiconductors with organic compounds has not been explored so extensively. In studies pertaining to dye-sensitized PEC cells (involving the use of high band gap semiconductors), the major objective had been of extension in the light absorption to the visible range. The role of organic compounds, especially the polymers, attached to the metal oxide semiconductors, in promoting the kinetics of electron-hole separation and charge carrier transport is still not well understood and needs thorough systematic investigation. Present proposal primarily aims to throw greater insight on this very vital aspect. Additionally, the researcher plans to compare the promotional role of chosen polymers vis-à-vis few prominent dye sensitizers in PEC water splitting.

The research group of the proposed supervisor in the department of Chemistry (DEI) is actively pursuing research in the area of PEC water splitting for the last 15 years. They have successfully completed several funded research projects (worth 3.5 crores), including a DST-NSF Indo-US project in collaboration with University of Maryland (USA), and a DST Consortium based project with five other Indian Institutes (IIT Kanpur, IIT Madras, BARC Mumbai, CECRI Karaikudi and IIT Rajasthan). Besides, an ongoing BRNS (Dept. of Atomic Energy) Project; this year the research group has been sanctioned, by the Govt. of India, another Indo-US project in collaboration with University of Arizona (USA) under "21st Century Knowledge Initiative Scheme" of UGC. Hugely benefited by these liberal funding from various governmental agencies, the research group has

developed a reasonably good infrastructure and instrumental support to work in the area of PEC water splitting. Table 1 depicts the facilities that exist in the department of Chemistry and elsewhere in the Institute to support the proposed plan of work.

Table 2

List of facilities/equipment available with the research group and elsewhere in the Institute to support the proposed plan of work

SL. No.		Facility/Equipment
1.	(a) Available within research group of the proposed supervisor	1. X Ray Diffraction Unit (Bruker AXS) 2. Scanning Electron Microscope (Table top) 3. Atomic Force Microscope (Nanosurf) 4. Thin Film Surface Profilometer 5. UV-Vis Spectrophotometer (Shimadzu) 6. IPCE measurement unit 7. UV-Vis light Source (Oriel) 8. Gas Chromatograph (Perkin Elmer) 9. Solar Simulator (Oriel) 10. High Temperature Muffle Furnace 11. Variable Power Supply 12. 150 W Tungsten Lamp 13. Vacuum Coating Unit 14. Spin Coating Unit 15. Spray- Pyrolysis Set-up 16. Cutter and Polisher 17. Potentiostat 18. LCR Meter 19. Single Pan Electronic Balance
2.	(b) Available elsewhere in the Dept. of Chemistry	1. Gas Chromatograph 2. FTIR Spectrometer 3. HPLC 4. HPTLC
3.	(c) Available elsewhere in the Institute	1. Glass-blowing facility 2. Electronic Repair Facility

3. Proposed Study

Proposed study deals with a comparative investigation on the promotional effect of surface modifications induced in nano-hetero-structured (bi-layered) thin films of metal oxides by some chosen intrinsically conducting polymers vis-à-vis selected dye sensitizers. The goal here would be to first synthesize nano-hetero-structured (bi-layered) thin films of metal oxides on conducting glass substrate, and then induce surface modifications in the top layer by coating/depositing a thin layer of some chosen intrinsically conducting polymers/dyes. The films, thus obtained, would be subjected to thorough characterization and their use in PEC water splitting would be investigated.

4. Objectives/Stages of the Proposed Study

- Wet chemical synthesis by sol-gel spin – coating of nano-hetero-structured (bi-layered) thin films of CuO – ZnO.
- Surface modifications of the prepared nano-hetero-structured (bi-layered) thin films of CuO-ZnO by loading the top layer with: (i) chosen intrinsic conducting polymers (Polypyrrole, and Polythiophene) (ii) selected dye sensitizers (Methylene Blue and Eosin). Selection is based on their absorption in the visible region and associated redox properties).
- The characterization of films for crystallographic, morphological and other semiconductor properties relevant to PEC water splitting.
- Studies on PEC water splitting using the films prepared and measurement of the PEC cell photocurrent and other performance indicators.

5. Proposed Methodology

Conducting glass plates will be used as substrate for the synthesis of bi-layered nano-hetero-structured thin films of metal oxides (CuO – ZnO). Films would be prepared by wet chemical method, sol-gel spin- coating. Sintering at high temperature would enable the evolution and growth of the desired crystalline phase. Chemical oxidative polymerization route would be followed to synthesize polymers, polypyrrole and polythiophene (Chitte et al. and Gok et al.). The polymer powder, thus obtained would be dispersed in a suitable solvent and subjected to spin-coating on bi-layered thin films of metal oxides. In experiments where surface modification of thin films samples by dye sensitizers is planned, films would be soaked in dye solution (taken in a suitable solvent) for optimized fixed duration, after which these would be dried in a furnace. After systematic and thorough characterization of the film samples, these would be subjected to PEC studies to explore their performance towards water splitting. Replicate measurements would reveal the reproducibility of the results and also verify the stability of the film samples over long-durations.

6. Tentative Plan of the Work

A tentatively drawn outline/plan of the proposed work has been presented in Table 3 along with a flow-chart (Fig.2), depicting the planned series of experiments.

7. Importance of the work and expected outcome

In order to achieve the ultimate goal of commercially viable PEC water splitting device for hydrogen generation (with estimated threshold device current density ≈ 10 mA/cm^2), research in this most vital area should continue in parallel on both the aspects, i.e. (i) fundamental research, exploring still obscure and hidden aspects of the phenomenon and (ii) technology development. The proposed study falls into the first category, as it is aimed towards the exploration of the promotional effects of some chosen intrinsically conducting polymers vis-à-vis few prominent dye sensitizers in electron-hole separation and charge carrier transport in nano-hetero-structured (bi-layered) thin films of metal oxide semiconductors, while using these as electrode in PEC water splitting. The study is expected to yield greater insight on this so far a grey area of knowledge and the obtained results may be exploited in future to generate an efficient PEC water splitting device for solar-hydrogen generation.

Table 3

Tentative outline of the proposed study.

	Stage I: Synthesis of samples (Bi-layered nano-hetero-strucutured thin films of metal oxide semiconductors)		
	Proposed parameters of the study		***Justification/Description***
	Materials of interest	High band gap: ZnO Low/moderate band gap: CuO	Bi-layered structures with a combination of low and high band gap materials would enable the maximum absorption of solar flux.
	Proposed method for Preparation	Wet chemical route (sol-gel spin coating)	Proposed chemical route is simple, cost-effective and can easily be up-scaled if desired.
	Variables	Film thickness (to be varied by varying the number of depositions)	Film thickness is a critical variant in this study.
	Stage II: Proposed surface modifications		
	Intrinsic conducting polymers	Polypyrole and Polythiophene	Intrinsic conduction property of chosen materials in expected to facilitate the charge carrier separation and transport.
	Dye sensitizers	Methylene Blue and Eosin.	Selection is based on their absorption in the visible region and associated redox properties.
	Stage III: Samples' characterization Samples prepared under stages 1 and 2 would be subjected to following characterizations.		
	Proposed parameters of the study		***Justification***
	▪ Phase analysis and crystallite size ▪ Microstructural details ▪ Surface morphology ▪ Surface Topography ▪ Optical properties (Band gap energy) ▪ Film thickness ▪ Charge carrier density ▪ Electrical resistivity ▪ Flatband potential	▪ X-ray Diffraction analysis ▪ X-ray Diffraction analysis ▪ Scanning Electron Microscopy ▪ Atomic Force Microscopy ▪ UV-Visible Spectroscopy ▪ Surface profilometer ▪ Mott Schottky plots ▪ Current – voltage plots ▪ Mott Schottky plots	The methods/ techniques proposed are standard and reliable.
	Stage IV: Measurements on photoelectrochemical (PEC) water splitting Samples prepared under stages 1 and 2 would be subjected to following measurements.		
	Proposed parameters of the study		***Justification/Description***
	PEC measurement variables	▪ Current-Voltage relationships and IPCE measurements under darkness and illumination. ▪ Photovoltage ▪ Photocurrent ▪ Open circuit potential ▪ Short Circuit current	Under controlled illumination and laboratory conditions, the PEC performance of the material systems synthesized would be evaluated.

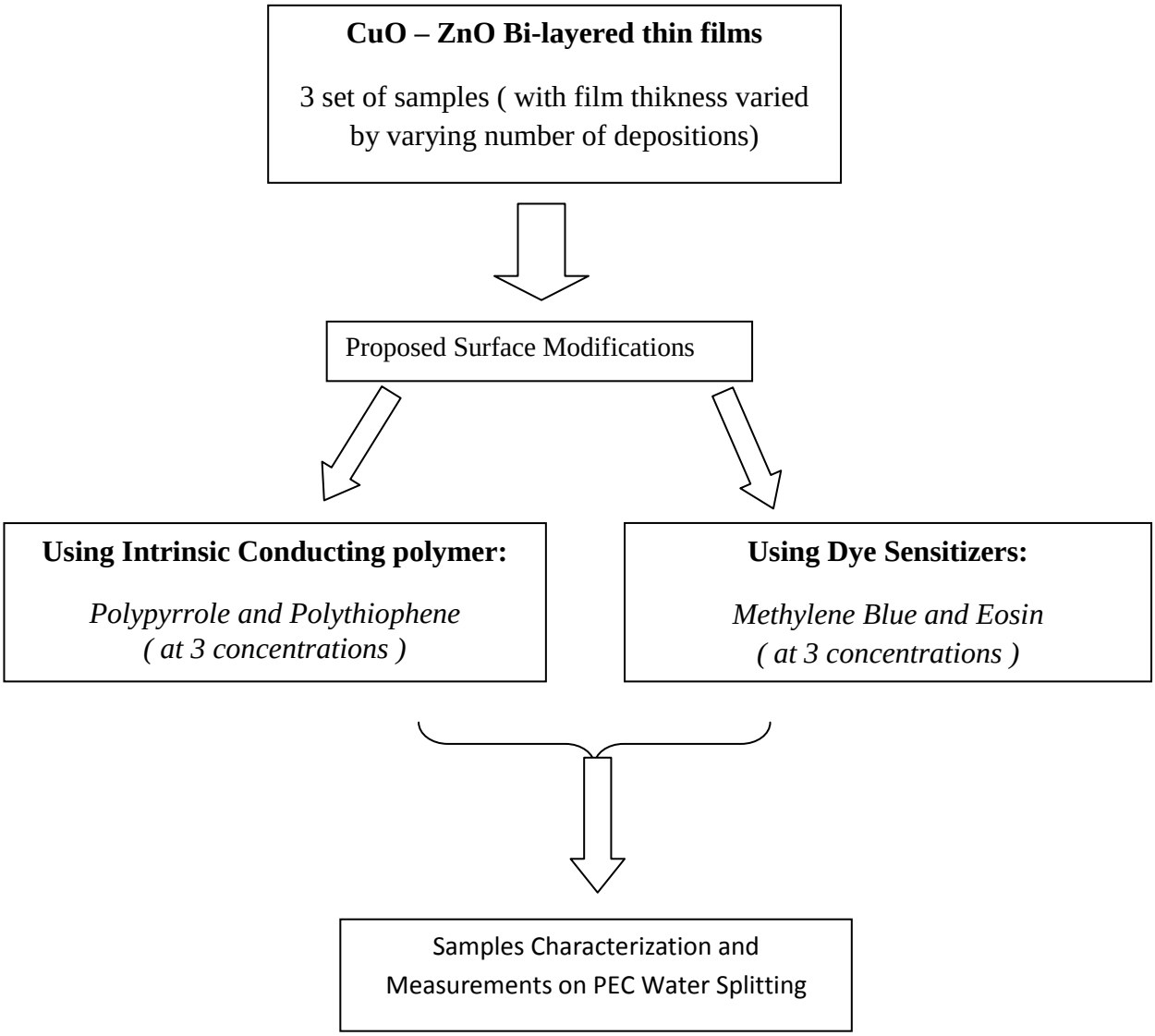
CuO – ZnO Bi-layered thin films
3 set of samples (with film thikness varied by varying number of depositions)
Proposed Surface Modifications
Using Intrinsic Conducting polymer:
Polypyrrole and Polythiophene (at 3 concentrations)
Using Dye Sensitizers:
Methylene Blue and Eosin (at 3 concentrations)
Samples Characterization and Measurements on PEC Water Splitting

Fig. 2: Planned Series of Experiments: A Flow Chart

Appendix 1
Literature Survey - Highlight

Presented below is the highlight of significant researches published in recent years in the proposed area of research.

Joshi et. al. (2015) reported that conjugated polymer nanodots can be used for biosensing and bioimaging. Polymer nanodots served as fluorophores and had fluorescent properties. They also synthesized nanodot embedded silica nano particles and characterization these with various technique. Polymer core retained its fluorescence properties and encapsulated silica facilitated easy modification with other functional groups.

Johra et. al. (2015) reported different chemical routes for the reduction of graphene oxide. The present study accounted for the production of reduced graphene oxide composite with zinc oxide and titanium oxide via hydrothermally reducing graphene oxide in de-ionized aqueous solution of TiO_2 and ZnO at 180 °C. The synthesized reduced graphene composite yielded 63% of photocatalytic activity for 2 hours associated with UV irradiation (100 W). The enhancement in comparison to pure ZnO was due to increased light absorption capacity and reduction in charge re-combination.

Krysa et. al. (2015) investigated the photocurrent density for TiO_2 and α-Fe_2O_3 prepared *via* two different methods: Sol-Gel and High Power Impulse Magnetron Sputtering. The comparative account for two oxides revealed that photocurrent density for TiO_2 under UV illumination is same while in case of α-Fe_2O_3 the photocurrent density is 10 times more in case of plasmatic films as compared to sol-gel derived films. The superiority of films is due to densely packed particles.

Myilsamya et. al. (2015) synthesized TiO_2 nano-composites doped with varying weights (in percentage) of In and Ce via sol-gel route and characterized for evaluation of different physical, morphological, topographical and functional parameters. Doping by 0.2 % weight of In and Ce caused the edges of the band to shift in the visible region. Cerium with the +4 oxidation state acted as a good abstracter of electron and had the tendency to transfer electron to adsorbed molecule for the production of oxygen, which led to the suppression of charge recombination.

Jushoa et. al. (2015) studied the activity of CuO – ZnO/MSN (MSN: meo-structured silica nanoarticles) catalyst, prepared at varying % weight of Cu and Zn. The characterization of prepared catalyst revealed the variation in number of Si-O-Si bond, oxygen vacancies, Si-O-Zn, and Si-O-Cu. All above manifestations, due to the variation in sequential addition of Cu and Zn over MSN, were important variant affecting the catalytic activity. Further, apart from the catalytic activity, the catalyst played crucial role in de-colorization of dye.

Gurudayal et. al. (2015) studied the Photoelectrochemical water splitting half reactions on Perovskite−Hematite tandem cells. The system possessed solar-to-hydrogen conversion efficiency of 2.4%. Hematite photoanode was prepared on FTO substrate in aqueous solution containing $FeCl_3 \cdot 6H_2O$ and urea were transferred into a teflon-lined autoclave. Fabrication of the perovskite was done by aerosol spray pyrolysis. These were characterized and subjected to PEC study.

Fernandesa et. al. (2015) investigated the hydrogen generation in presence and absence of Ru nanoparticles over the irregular and porous carbon films. Ru nanoparticles of size nearly 10 nm were deposited over the high surface area of carbon thin films *via* phase explosion at high laser influence. The hydrogen generation was reported to be six times to the hydrogen production *via* carbon films without Ru particle in ammonia borane hydrolysis. In addition to morphological characteristics, the presence of sp^2 bonded carbon atoms facilitated good scattering of nano-particles

and generated maximum number of catalytic active sites. On the other hand, the catalytic activity was found to decrease with increase in hydrolysis cycle.

Si. Mohamed et. al. (2015) reviewed properties of polythiophene and reported that it has thermal and chemical stability. The solubility properties depended on substitution at 3,5 position of thiophene ring, as it lad to increase in solubility of polymer. Polythiophene performed as a good material for solar cell. In accordance with that the experimentally measured bandgap for polythiophene was around 2.0–2.3 eV. It corresponded to energy maxima around at 400- 540 eV. The modification in chemical structures could greatly modify and improve the electronic and optical properties of polythiophene studied materials.

Kumar et. al. (2014) reported catalytic steam reforming of ethanol for hydrogen production, as ethanol is expected to yield maximum number of hydrogen per molecule as compared to water, methanol and methane. The catalyst developed by them played a positive role for the hydrogen generation, the effect comparable to the effects of certain noble metals and transition elements, which are reported as the efficient catalyst in literature for hydrogen generation.

Obaid et. al. (2014) synthesized polyaniline from electrodeposition process. They used stainless steel rods as the working electrode. Polyaniline was electrochemically synthesized from aqueous acidic solution containing aniline monomer by cycling the working electrode potential between −0.18 and 1 V. It was found that the nature of the voltammograms observed at different concentrations of acid, viz. 0.5 M and 1 M of H_2SO_4, were similar. Morphology of prepared polyaniline was examined by SEM and electrochemical parameters of the electrodeposited polyaniline were determined using cyclic voltammetry.

Tao Xu and Luping Yu (2014) has reported that polymer having band gap around 1.1 eV are capable of absorbing about 77% of solar energy and also discussed about four synthetic principles to engineer the band gap and the energy levels and the solubility of the targeted polymers .One of the method to reduce band gap is achieved by changing the ring orientation. Fluorination also affected the band gap by changing polymeric back. On replacing hydrogen by fluorine it led to the difference in dipole moment and HOMO - LUMO gap also got reduced. Substituent effect also led to change in band gap. Additives and branching enhanced the solubility of the polymer.

Boeva et al. (2014) has reported various properties of polyaniline. They observed that polyaniline can be used as electrode material but its conductivity reduces at neutral pH. It has wide applications in transparent antistatic coatings and solar batteries, flexible electrodes, organic field transistor, conducting fibers, and electromagnetic screens. Chemical polymerization of polyaniline takes place in presence of oxidant generally ammonium persulfate. Monomer of aniline and oxidant should be kept in contact under continuous stirring and the solution would turn green on polymer formation. They observed that chemical synthesis of polyaniline is the simplest way to prepare conducting polymers with various physicochemical properties.

Haiyan et. al. (2013) investigated conjugated polymers as ideal semiconductors for next generation low-cost electronics, as they combine interesting tunable electronic and optical properties with excellent solution processing and mechanical flexibility. Their structural properties were identified by XRD analysis; while optical absorption spectroscopy provided insight into the electronic structure of the conjugated polymer.

Chougule et al. (2012) synthesized polypyrrole by chemical oxidative polymerization technique. Reaction was carried out in a beaker by mixing 0.1 M aqueous solution of pyrrole and 0.1 M ammonium per-sulphate in 1:1 ratio by volume for 3 hours to allow polymerization to occur. Thin

films of polypyrrole were prepared by dissolving polypyrrole in m-cresol and cast using spin coating technique on glass substrates. Thin films of polypyrrole were characterized by X ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infra red spectroscopy (FTIR), UV visible spectroscopy and electrical resistivity by four probe method.

Pacheco et. al. (2011) worked on composites of carbon and conducting polymer. Mesoporous carbon/conducting polymer composites were synthesized by adsorption of different monomers (aniline, pyrrole, thiophene and 3-methylthiophene) in the gas phase onto the carbon surface, followed by oxidative chemical polymerization. Electrochemical performance of the composites was studied by cyclic voltammetry and galvanostatic charge/discharge. All composite electrodes showed a stable cycle life in the potential range of 0 to 1V. The incorporation of the polymers to the carbon led to a decrease of the BET surface value and the decrease in pore volume.

Richard et. al. (2009) synthesized polythiophene (PTh) nanoparticles by cationic surfactant assisted dilute polymerization method using $FeCl_3$ as oxidant to use as electrode material for high performances redox supercapacitors. Surfactant (used was CBTA), oxidant ($FeCl_3$) and monomer were subjected to constant stirring for 24 hours when a brown coloured precipitate of polymer was obtained. The physical characterizations of the synthesized PTh nanoparticles were studied by FT-IR and UV-Visible spectroscopy, XRD and SEM. The synthesized PTh nanoparticles were used for the first time to fabricate symmetric type redox supercapacitor and its capacitor performances were studied by cyclic voltammetry and charge-discharge.

Wang et. al. (2008) studied synthetic photosynthesis polymer semiconductor. They reported that the first material studied for hydrogen evolution was poly (*p*-phenylene), but with ultraviolet light only and it also suffered with rapid decomposition under irradiation. Covalent carbon nitrides also have great potential, as their mesoporous structure works as heterogeneous catalyst. Light

harvesting ability of the material increases due to its large surface. The effect of optimizing nanostructure in dye-sensitized mesoporous TiO_2 solar cell was found to improve the cell performance by almost hundred times as compared with a cell based on a bulk TiO_2 electrode. Similarly, they studied that a metal-free mpg-C_3N_4 catalyst, when appropriately modified by polymer, holds the greatest promise for visible light photocatalysis, as its conversion performance of solar to hydrogen is around 7%.

Rongliang et. al. (2008) investigated the kinetics of photocatalytic degradation of phenol using conjugated polymer sensitized TiO_2 and ZnO. Both TiO_2 and ZnO mainly absorb in UV region, but polymer sensitized semiconducting material and PFT modified semiconductor depicted absorption shift to the visible region. By changing different variable such as initial concentration of phenol, dosage of the photocatalyst, and the pH value, the rate of photodegradation of phenol varied and was reported.

Ansari (2006) reviewed polypyrrole. He reported various application of polypyrrole. Polypyrrole and wide range of its derivatives can be prepared by oxidative polymerization method. Other simple methods are electrochemical method and chemical vapor deposition. Polypyrrole can be formed in aqueous and non aqueous media. Polymer formed by electrosynthesis allows an easy control of the thickness of the polymer films, but it need control over various reaction condition such as pH, cell conditions, the solvent, electrode, applied potential and temperature which were not easy to maintain. He also studied the electrical conductivity of the polypyrrole films which are strongly influenced by the preparation conditions such as the nature/concentration of electrolyte, doping level, current density, synthesis temperature, and solvent.

Baibarac et. al. (2006) explored the use of polymer and carbon nanotube composites in super capacitor devices. They studied two methods of synthesis of polyn-vinyl carbazole (PVK)/CN

composites; one was direct mixing of the polymer with CNs, and other is chemical polymerization of monomer in the presence of carbon nanoparticles. Poly N-vinyl carbazole (VK)/carbon nanotube (CN) films were studied by cyclic voltammetry in $LiClO_4$/acetonitrile solution. Characterization was done by Raman scattering and UV–VIS–NIR spectroscopic studies.

Hwang et. al. (2006) reported pH-induced ion transport in polypyrrole. Polypyrrole was prepared by chemical vapour deposition method. They adjusted the pH of the solution from 6.8 to11.9 by adding $HClO_4$ and hydroxides (NaOH, KOH, CsOH). They observed that polypyrrole becomes insulating in a basic solution. Polypyrrole showed its conductive properties at acidic pH. At basic pHs, it led to precipitate in solution and amount of precipitation measured its diminished conductivity.

Young et. al. (2005) prepared polyaniline with electrodeposition method and studied their topographical and electrical properties with current-sensing atomic force microscope. Doped polyaniline films prepared in 0.30 M nitric acid were conductor with an average conductivity of 49 S/cm. On varying pH, as the proton activity goes down elactrochemical properties were also reduced.

Vishnuvardhan et. al. (2005) reported synthesis of conductive polymer composites of polypyrrole/yttrium oxide by oxidative polymerization method and varied weight percent of oxide for different samples. They used $FeCl_3$ as oxidant. Electrical conductivity of pallet depended on the concentration of Y_2O_3 in the composite. The synthesized polymer composites were characterized by infrared and X-ray diffraction techniques. The surface morphology of the composite was studied by scanning electron microscopy.and other chrecterisation techniques.

Yong et. al. (2004) employed chemical method to prepare ω-sulfonated polystyrene-stabilized cadmium sulfide (CdS) nanoclusters. The ω-sulfonated polystyrene (Mn = 5000 g/mol) was prepared successfully through chain-end sulfonation of poly (styryl) lithium using 1,3-propanesulfone.stablizing reagent for the preparation mixture of toluene and methanol (9:1, v/v). ω-sulfonated PS-stabilized CdS nanoclusters were found stable in air and can be readily re-dissolved in the hydrocarbon or polar solvents such as toluene, tetrahydrofuran (THF), or chloroform. Nanoclusters were characterized by a combination of transmission electron microscopy, X-ray diffraction, and UV/Vis spectroscopic analysis.

Hikmat et. al. (2002) studied Tetra (-4-pyridyl) porphyrinatomanganese (III) sulfate (as an Mn III^{+}, Mn II ion mixture), embedded into a polysiloxane polymer matrix and attached to the surfaces of the n-GaAs electrode. The n-GaAs/polymer/MnP system was annealed under nitrogen and used for a photoelectrochemical study in a water/$LiClO_4$/$Fe(CN)_6-$ /$Fe(CN)_4-$ system. The values of short-circuit currents, measured after minutes of illumination, were significantly enhanced by modification. The modified electrode surfaces were more stable to degradation, in the dark and under illumination, than the unmodified ones. The modified electrodes showed higher light-to-electricity conversion efficiency than the unmodified ones. Generally polymer electrode suffers from peeling off of organic layer. In this case the polymer layer adhered perfectly to the semiconductor surface without peeling off. Due to annealing it till 100 ºC the modified n-GaAs surface added further enhancement to its characteristics.

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